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1. Untranslatable words are replaced with asterisks (****).
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FULL CONTENTS

[Claim(s)]

[Claim 1]A fluorine content compound which has one or more -CF₂-units and (meta) acryl groups in the following components (A) - (C):(A) one molecule;

(B) Silica sol with a grain size of 60 nm or less; And an activity energy line hardenability constituent containing the (C) polymerization initiator.

[Claim 2]In a manufacturing method of a layered product with which a hardening resin layer was provided on a substrate, A process of forming on a substrate an activity energy line hardenability layer which consists of the following processes (a) and an activity energy line hardenability constituent given in (b):(a) Claim 1; [and by irradiating with an activity energy line an activity energy line hardenability layer formed at the (b) process (a)] A manufacturing method including a process of forming a hardening resin layer which a silica gel distributed in a fluorine content (meta) acrylate polymer.

[Claim 3]A layered product obtained by the manufacturing method according to claim 2.

[Detailed Description of the Invention]**[0001]**

[Field of the Invention]This invention relates to the manufacturing method of the layered product which used an activity energy line hardenability constituent and it. In more detail, a low refractive index and abrasion-proof nature are shown, and, moreover, it is related with the manufacturing method of a layered product using an activity energy line hardenability constituent and it with a long pot life and short hardening time.

[0002]

[Description of the Prior Art]In recent years, the antireflection function is mentioned as one of the demand performances in an image display board. The principle of a general antireflection function provides a low refractive index layer on the surface of a high refractive index layer, and reduces a reflected light by making

the light reflected by a high refractive index layer, and the light reflected by a low refractive index layer interfere mutually using those optical path differences.

[0003] Although such a coating was conventionally produced by vacuum deposition, since the manufacturing cost is high, these days, it is formed using the wet coating technique from which the thin film of low cost is obtained comparatively. Here, when forming a low refractive index layer by wet coating technique, generally as a coating composition for it, the mixture of silica sol and alkoxy silane is used.

[0004] However, abrasion-proof nature comes out enough and the low refractive index layer formed from the mixture has the fault that the reflectance of a certain coating average produced with vacuum deposition on the other hand is not obtained.

[0005] [I then by using the mixture of fluorine atom content organosilane and fluorine content silyl group content vinyl polymer as a coating composition for low reflectance layer formation] A wide range wavelength area shows a low reflectance uniformly, and obtaining the coating which was simultaneously excellent in film strength, endurance, soil-proof adhesion, and a heat-resisting property is proposed (JP,H11-106704,A).

[0006]

[Problem to be solved by the invention] However, it is taken for the thermosetting composition which generally makes organosilane a principal component to have the problem that a pot life is short, and to harden it moreover, in order that a reaction may progress gradually also during the preservation for several hours, and also has the problem that productivity is low.

[0007] The purpose of this invention is to provide the constituent suitable for especially formation of a coating which a pot life is long, and short-time hardening is possible, and can give the low refractive index film which has abrasion-proof nature.

[0008]

[Means for solving problem] Since the polymerization curing reaction does not advance unless the activity energy line hardenability constituent which generally contains the acrylate (meta) hardened with activity energy lines, such as ultraviolet radiation, as a principal component irradiates with an activity energy line, [this invention persons] Once a very long pot life is shown compared with silicone series heat-curing resin and it moreover irradiates with an activity energy line, in order to harden for a short time (for example, the inside and outside of several seconds), [by using the compound which introduced at least one or more -CF₂-units into the acrylate which is a principal component (meta) in view of the point which shows high productivity] The long activity energy line hardenability constituent with short hardening time was obtained, and moreover, from the constituent, the pot life found out that the hardening resin film in which a low refractive index and good abrasion-proof nature are shown could be obtained, and completed this invention.

[0009] Namely, fluorine content compound in which this invention has one or more -CF₂-units and (meta) acryl groups in the following components (A) - (C): (A) one molecule; (B) Silica sol with a grain size of 60 nm or less; And an activity energy line hardenability constituent containing the (C) polymerization initiator is provided.

[0010] In the manufacturing method of a layered product with which the hardening resin layer was provided

on the substrate as for this invention, Process of forming on a substrate the activity energy line hardenability layer which consists of the following processes (a) and the (b): (a) above-mentioned activity energy line hardenability constituent; [and by irradiating with an activity energy line the activity energy line hardenability layer formed at the (b) process (a)] A manufacturing method including the process of forming the hardening resin layer which the silica gel distributed in a fluorine content (meta) acrylate polymer, and the layered product obtained by this manufacturing method are provided.

[0011] In this Description, an acrylate group (meta), acrylic acid, or methacrylic acid is called [an acrylyl group or a methacryloyl group] acrylic acid (meta) for an acrylyl group (meta), and an acrylate group or a methacrylate group.

[0012]

[Mode for carrying out the invention] The activity energy line hardenability constituent of this invention contains the component (A) fluorine content compound, component (B) silica sol, and a component (C) polymerization initiator.

[0013] [the fluorine content compound of the component (A) used by this invention] It is a compound which has one or more $-CF_2-$ units (namely, difluoro methylene unit) and acrylyl groups (meta) in one molecule, and has a $-CF_2-$ unit in the alcohol residue side of acrylate (meta) preferably.

[0014] [as such a fluorine content compound being concrete] 2,2,2-trifluoroethyl (meta) acrylate, 2,2,3,3-tetrafluoro propyl (meta) acrylate, 1H, 1H, 5H-octafluoropentyl (meta) acrylate, 2,2,3,4,4,4-hexafluoro butyl (meta) acrylate, Perfluoro ethyl (meta) acrylate, 2,2,3,3,4,4,5,5-octafluoro hexane-1,6-di(meth)acrylate, 1H,1H,8H,8H-trideca fluoro octane (meta) acrylate, etc. are mentioned. When enlarging film strength of the hardening resin layer after a polymerization, [in these] It is preferred to use polyfunctional (meta) acrylate and especially the molecular weight between crosslinking points (mass average) can use preferably the suitable 2,2,3,3,4,4,5,5-octafluoro hexane-1 and 6-di(meth)acrylate in respect of abrasion-proof nature.

[0015] [content in solid content (all the components except a diluent when a diluent is used) of an activity energy line hardenability constituent of a fluorine content compound] Since abrasion-proof nature will fall if too large [if too small, it will become a high refractive index, and], more than 40 mass % is [more than 20 mass % / below 80 mass %] below 70 mass % more preferably.

[0016] In this invention, in order to raise the abrasion-proof nature of a hardening resin layer, silica sol is used as a component (B). As silica sol, a grain size uses 60 nm or less of 20-40-nm things [1-50 nm of] more preferably. This is because a haze value of an activity energy line hardenability constituent will become high, transparency will be lost and it will moreover become easy to drop out after membrane formation of the surface, if a grain size exceeds 60 nm.

[0017] In a process of forming an activity energy line hardenability layer on a substrate, silica sol will be transferred to a gel, and will exist in a hardening resin layer as a silica gel.

[0018] [content in solid content (all the components except a diluent when a diluent is used) of an activity energy line hardenability constituent of silica sol] Since it will become a weak film if too large [if too small, abrasion-proof nature will fall, and], more than 30 mass % is [more than 20 mass % / below 80 mass %]

below 60 mass % more preferably.

[0019]In this invention, it can choose suitably as a polymerization initiator of a component (C) according to the kinds (ultraviolet radiation, visible light, electron rays, etc.) of activity energy line which is a curing means. For example, when performing photopolymerization, it is preferred to make one or more kinds of publicly known photocatalyst compounds which use a photopolymerization initiator, in addition are chosen from a photosensitizer, an optical accelerator, etc. contain.

[0020]As an example of a photopolymerization initiator, 2,2-dimethoxy- 2-phenylacetone, Acetophenone, benzophenone, a xantho fluorenone, benzaldehyde, Anthraquinone, 3-methylacetophenone, 4-chlorobenzo phenon, 4,4-diaminobenzophenone, benzoin propyl ether, benzoin ethyl ether, Benzyl dimethyl ketal, 1-(4-isopropylphenyl)-2-hydroxy-isobutane 1-ON, 4-thioxan ton, camphor quinone, and 2-methyl-1-[4-(methylthio) phenyl]-2-morpholinopropane 1-ON etc. are mentioned. The photopolymerization initiator which has at least one acryl group (meta) can also be used for intramolecular like N-acryloyloxy ethylmaleimide.

[0021]As for the content in the solid content (all the components except a diluent when a diluent is used) of the activity energy line hardenability constituent of a photopolymerization initiator, more than 3 mass % is [more than 0.1 mass % / below 10 mass %] below 5 mass % more preferably.

[0022]In this invention, in order to promote photopolymerization, a photosensitizer may be used with a photopolymerization initiator. As an example of a photosensitizer, 2-chloro thioxan ton, 2,4-diethylthio xanthone, a 2,4-disopropyl thioxan ton, etc. can be mentioned.

[0023]In this invention, in order to promote photopolymerization, an optical accelerator may be used with a photopolymerization initiator. As an example of an optical accelerator, p-dimethylamino ethyl benzoate, p-dimethylamino isoamyl benzoate, p-dimethylaminobenzoic acid 2-n-butoxy ethyl, 2-dimethylaminoethyl, benzoate can be mentioned.

[0024]In the activity energy line hardenability constituent of this invention, the ethylenic unsaturated compound, the vinyl ether compound, epoxy compound, and oxetane compound which can polymerize with an activity energy line can be used together if needed.

[0025]If it is considered as the example of an ethylenic unsaturated compound (meta), acrylic acid; methyl (meta) acrylate, Ethyl (meta) acrylate, propyl (meta) acrylate, n-butyl (meta) acrylate, t-butyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, n-nonyl (meta) acrylate, cyclohexyl (meta) acrylate, Benzyl (meta) acrylate, JISHIKURO pentenyl (meta) acrylate, 2-JISHIKUROPENTENOKISHI ethyl (meta) acrylate, glycidyl (meta) acrylate, Methoxy ethyl (meta) acrylate, ethoxyethyl (meta) acrylate, Butoxy ethyl (meta) acrylate, methoxy ethoxyethyl (meta) acrylate, Ethoxy ethoxyethyl (meta) acrylate, tetrahydrofurfuryl (meta) acrylate, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, 4-hydroxy butyl (meta) acrylate, phenoxyethyl (meta) acrylate, phenoxyethoxyethyl (meta) acrylate, biphenoxy ethyl (meta) acrylate, Biphenoxy ethoxyethyl (meta) acrylate, norbornyl (meta) acrylate, Phenylepoxy (meta) acrylate, acryloyl morpholine (meta), N-[2-(meta) acryloyl ethyl]-1,2-cyclohexanedicarboimide, N-[2-(meta) acryloyl ethyl]-1,2-cyclohexanedicarboimide 1-ene, Monofunctional nature (meta) acrylate system monomers, such as N-[2-(meta) acryloyl ethyl]-1,2-cyclohexanedicarboimide 4-ene; N-vinyl pyrrolidone, N-vinylimidazole, N-

vinylcaprolactam, styrene, alpha-methylstyrene, Vinyl system monomer;1, such as vinyltoluene, allyl acetate, vinyl acetate, vinyl propionate, and vinyl benzoate, 4-butanediol di(metha)acrylate, 1,6-hexanediol di(metha)acrylate, 1,9-nonane JIORUJI (meta) acrylate, Neopentyl glycol di(metha)acrylate, neopentyl glycol pivalate S TERUJI (meta) acrylate, ethylene glycol di(metha)acrylate, poly ethylene glycol di(metha)acrylate Triethylene glycol di(metha)acrylate, poly propyleneglycol di(meth) acrylate, Bisphenol A-diglycidyl ETERUJ (meta) acrylate, Bisphenol A-JIEPOKISHIJI (meta) acrylate, ethyleneoxide denaturation bisphenol A-di (meth)acrylate, Ethyleneoxide denaturation diacrylate of 1,4-cyclohexane dimethanol, Ethyleneoxide denaturation tetrabromobisphenol A-di(meth)acrylate, 2 functionality (meta) acrylate, such as zinc diacrylate Trimethylolpropane bird (meta) acrylate, D trimethylol propanetetra (meta) acrylate, pentaerythritol tetra (meta) acrylate, Pentaerythritol penta (meta) acrylate, pentaerythritol hexa (meta) acrylate, The bird (meta) acrylate of ethyleneoxide addition trimethylolpropane, the tetra (meta) acrylate of ethyleneoxide addition ditrimethylol propane, the bird (meta) acrylate of propylene oxide addition trimethylolpropane, Ethyleneoxide denaturation isocyanuric acid bird (meta) acrylate, The tetra (meta) acrylate of propylene oxide addition ditrimethylol propane, The tetra (meta) acrylate of ethyleneoxide addition pentaerythritol, The tetra (meta) acrylate of propylene oxide addition pentaerythritol, Dipentaerythritol penta (meta) acrylate, the penta (meta) acrylate of ethyleneoxide addition dipentaerythritol, The penta (meta) acrylate of propylene oxide addition dipentaerythritol, Dipentaerythritol hexa (meta) acrylate, the hexa (meta) acrylate of ethyleneoxide addition dipentaerythritol, The hexa (meta) acrylate of propylene oxide addition dipentaerythritol, Bird allyl cyanurate, triallyl isocyanurate, bird allylformal, Polyfunctional monomers of three or more organic functions, such as 1,3,5-bird acryloyl hexahydro s-hydrazine; oligomer acrylate, such as urethane acrylate and ester acrylate, etc. are mentioned. The polyfunctional monomer of two or more organic functions is used preferably among these. These compounds are used by independent or two sorts or more.

[0026]As an example of a vinyl ether system compound, ethyleneoxide denaturation bisphenol A-divinyl ether, Ethyleneoxide denaturation bisphenol F-divinyl ether, ethyleneoxide denaturation catechol divinyl ether, Ethyleneoxide denaturation resorcinol divinyl ether, ethyleneoxide denaturation hydroquinone divinyl ether, ethyleneoxide denaturation-1, 3 and 5, and benzenetriol bird vinyl ether are mentioned.

[0027]As an example of epoxy compound, 1,2-epoxy cyclohexane, 1,4-butanediol diglycidyl ether and 3,4-epoxycyclohexylmethyl 3' and 4'-epoxy cyclohexane carboxylate, Glycidyl ether of trimethylolpropane diglycidyl ether, bis(3,4-epoxy-6-methylcyclohexyl methyl)Aji Pate, and phenol novolak and bisphenol A diglycidyl ether are mentioned.

[0028]As an example of an oxetane compound, 3-ethyl-3-hydroxymethyloxetane, 3-ethyl-3-(phenoxyethyl) oxetane, JI [1-ethyl (3-oxetanyl)] methyl ether, 3-ethyl-3-(2-ethylhexyloxymethyl) oxetane, etc. are mentioned.

[0029]A diluent whose coating becomes it is thin (preferably 0.01-micrometer or more thickness of 10 micrometers or less), and possible about the activity energy line hardenability constituent is used for the activity energy line hardenability constituent of this invention. The amount of the diluent used can be suitably determined according to the thickness of the hardening resin layer made into the purpose.

[0030] If it is the diluent used for the common plastic paint as such a diluent, there will be no restriction in particular, but. For example, ketone system compounds, such as acetone, methyl ethyl ketone, and cyclohexanone; Methyl acetate, Ester system compounds, such as ethyl acetate, butyl acetate, ethyl lactate and acetic acid methoxy ethyl; Diethylether, Ethylene glycol wood ether, ethylcellosolve, butyl cellosolve, Ether system compounds, such as phenyl cellosolve and dioxane; Toluene, Aromatic compounds, such as xylene; alcohol compounds, such as halogen system hydrocarbon; methanol, such as aliphatic compound; methylene chlorides, such as pentane and hexane, chlorobenzene, and chloroform, ethanol, normalpropanol, and isopropanol, water, etc. can be mentioned.

[0031] In the activity energy line hardenability constituent of this invention, polymerization inhibitor, a defoaming agent, a leveling agent, a dispersant, a plasticizer, an antistatic agent, a surface active agent, nonresponsive polymer, etc. can be further added in the range which does not spoil the effect of this invention if needed.

[0032] The resin composition of this invention can manufacture component (A) - (C) explained above and other components blended if needed by mixing uniformly in accordance with a conventional method.

[0033] The activity energy line hardenability constituent of this invention can be preferably used on a substrate as a raw material of the hardening resin layer at the time of manufacturing the layered product by which the hardening resin layer was laminated at least. Such a layered product can be manufactured in accordance with a manufacturing method including the following processes (a) and (b).

[0034] Process (a)

First, the activity energy line hardenability layer which consists of an activity energy line hardenability constituent of this invention is formed on a substrate. On a substrate, specifically, [the activity energy nature hardenability constituent of this invention] A coating method using the roll used by the impregnating method Toppan Printing, monotonous printing, intaglio printing, etc., It coats by a spray method, the curtain flow coa method, etc. which are sprayed on a substrate, and an activity energy line hardenability layer is formed by carrying out heating evaporation removal of the low boiling material, such as a diluent, using a heating furnace, a far-Infrared furnace, or a super-far-infrared furnace if needed.

[0035] As a substrate, plastic substrates, such as metal boards (iron, an aluminium, etc.) of tabular or the shape of a film, a ceramic substrate containing a glass substrate, an acrylate resin, PET, and polycarbonate a hardening resin board, etc. can be used.

[0036] Process (b)

Next, the silica gel which silica sol gelled forms the hardening resin layer dispersed to the polymer of the fluorine content compound by irradiating with an activity energy line the activity energy line hardenability layer formed at the process (a). The layered product which has by this the hardening resin layer which was excellent in the low refractive index at abrasion-proof nature can be obtained by low cost.

[0037] The layered product produced by doing in this way was not restricted to two-layer structure, may provide beforehand the layer of the material of thermoplasticity, thermosetting, and optical hardenability, or may provide it anew after hardening resin layer formation. For example, if a high refractive index layer is

provided on the hardening resin layer of this layered product, it will become available as a coating.

[0038]Although wide range activity energy lines, such as ultraviolet radiation, a visible radiation, a laser, electron rays, and X-rays, can be used as an activity energy line, it is preferred also in these to use ultraviolet radiation from a practical use side. As a concrete ultraviolet radiation source, a low pressure mercury lamp, a high pressure mercury lamp, a xenon lamp, a metal halide lamp, etc. are mentioned.

[0039]

[Working example]Hereafter, although this invention is concretely explained based on an embodiment, this invention is not limited to this.

[0040]Colloidal silica with embodiment 1 grain size of 10-20 nm (trade name) [MEK-ST and] Nissan Chemical Industries, Ltd. make 3 mass part (solid content conversion), the 2,2,3,3,4,4,5,5-octrafluoro hexane- 1, 6-diacylate (product made from Central Medicine) 7 mass part, Photopolymerization Initiator (IRGACURE 184, Ciba-Geigy make) 0.5 mass part and methyl-ethyl-ketone 90 mass part were mixed, and the activity energy line hardenability constituent was obtained. When this constituent was kept with the well-closed container under the room temperature, deterioration was not accepted even after passing on the 30th.

[0041]It applied on the acrylic board and the obtained activity energy line hardenability constituent was dried so that it might be set to 0.1 micrometer or 3 micrometers by dry membrane thickness, and the activity energy line hardening layer was formed. Then, the laminated sheet was produced by irradiating with ultraviolet radiation for 30 seconds from a high pressure mercury lamp, and forming a hardening resin layer to an activity energy line hardening layer.

[0042]It replaces with the embodiment 22,2,3,3,4,4,5,5-octrafluoro hexane- 1 and 6-diacylate 7 mass part, [except using 1H, 1H, and 5H-octafluoropentyl acrylate (made by OSAKA ORGANIC CHEMICAL INDUSTRY, LTD.) 6 mass part] The activity energy line hardenability constituent was prepared like Embodiment 1, and the hardening resin layer whose thickness is 0.1 micrometer and 3 micrometers, respectively produced the laminated sheet formed on the acrylic board.

[0043]When the obtained activity energy line hardenability constituent was kept with the well-closed container under the room temperature, deterioration was not accepted even after passing on the 30th.

[0044]Colloidal silica with comparative example 1 grain size of 10-20 nm (and) [trade name] The thermosetting composition was obtained by mixing Nissan Chemical Industries, Ltd. make 4 mass part (solid content conversion), methyl trimetoxysilane (trade name KBM13, Shin-Etsu Chemical Co., Ltd. make) 6 mass part, and acetic acid 0.1 mass part, and ripening for four days.

[0045]The obtained thermosetting composition was applied on the acrylic board so that it might be set to 0.1 micrometer or 3 micrometers by dry membrane thickness, and 0.1 micrometer in thickness and a 3-micrometer hardening resin layer produced the laminated sheet formed on the acrylic board by heating at 60 ** for 4 hours.

[0046]When the obtained thermosetting composition was kept with the well-closed container under the room temperature, the precipitate was accepted after progress on the 30th.

[0047] The comparative example 22,2,3,3,4,4,5,5-octafluoro hexane- 1, 6-diacylate (product made from Central Medicine) 10 mass part, Photopolymerization initiator (IRGACURE 184 Ciba-Geigy make) 0.5 mass part and methyl-ethyl-ketone 90 mass part were mixed, and the activity energy line hardenability constituent was obtained. The obtained activity energy line hardenability constituent was used, and the hardening resin layer whose thickness is 0.1 micrometer and 3 micrometers like Embodiment 1, respectively produced the laminated sheet formed on the acrylic board.

[0048] When the obtained activity energy line hardenability constituent was kept with the well-closed container under the room temperature, deterioration was not accepted even after passing on the 30th.

[0049] [I except replacing with colloidal silica with comparative example 3 grain size of 20-40 nm, and using grain size three mass parts (solid content conversion) of 70-100 nm (trade name ST-ZL, Nissan Chemical Industries, Ltd. make)] The activity energy line hardenability constituent was prepared like Embodiment 1, and the hardening resin layer whose thickness is 0.1 micrometer and 3 micrometers, respectively produced the laminated sheet formed on the acrylic board.

[0050] When the obtained activity energy line hardenability constituent was kept with the well-closed container under the room temperature, deterioration was not accepted even after passing on the 30th.

[0051] (Evaluation) The 5-degree normal reflectance of the hardening resin layer of the laminated sheet with which the hardening resin layer of 0.1 micrometer of thickness produced by each embodiment and a comparative example was formed concerned was measured, and the refractive index was calculated. The pencil hardness of the hardening resin layer of the laminated sheet with which the hardening resin layer of 3 micrometers of thickness was formed concerned was measured. The obtained result is shown in Table 1.

[0052]

[Table 1]

Embodiment comparative example 12 1 2 Refractive-index 1.372 of a 3 pencil-hardness 4H 4H 2H B B hardening layer 1.389 1.410 1.362 1.375 [0053] A pot life is long, short-time hardening is possible for the activity energy line hardenability constituent of Embodiments 1 and 2, and, moreover, the above result shows that the hardening resin layer after hardening shows a low refractive index and good abrasion-proof nature.

[0054] On the other hand, the hardenability constituent of an organosilane system of the comparative example 1 has a short pot life, preservation stability is missing, and prolonged hardening time is required, and the refractive index of the hardening resin layer after hardening is higher than Embodiments 1 and 2, and, moreover, it turns out that abrasion-proof nature is inferior. Although a pot life is long and short-time hardening was possible for the activity energy line hardenability constituent of the comparative example 2 which is not using silica sol, the abrasion-proof nature of the hardening resin layer after hardening was very bad. Although a pot life is long and short-time hardening was possible for the activity energy line hardenability constituent of the comparative example 3 which uses the thing of the grain size which greatly exceeds 60 nm as silica sol, the abrasion-proof nature of the hardening resin layer after hardening was very bad.

[0055]

[Effect of the Invention] The activity energy line hardenability constituent of this invention has a long pot life, short-time hardening is possible, and the hardening resin film which moreover has abrasion-proof nature with a low refractive index can be given. Therefore, it can use in favor of the coating used for a display screen protection plate etc.

[Translation done.]